

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
3 June 2004 (03.06.2004)

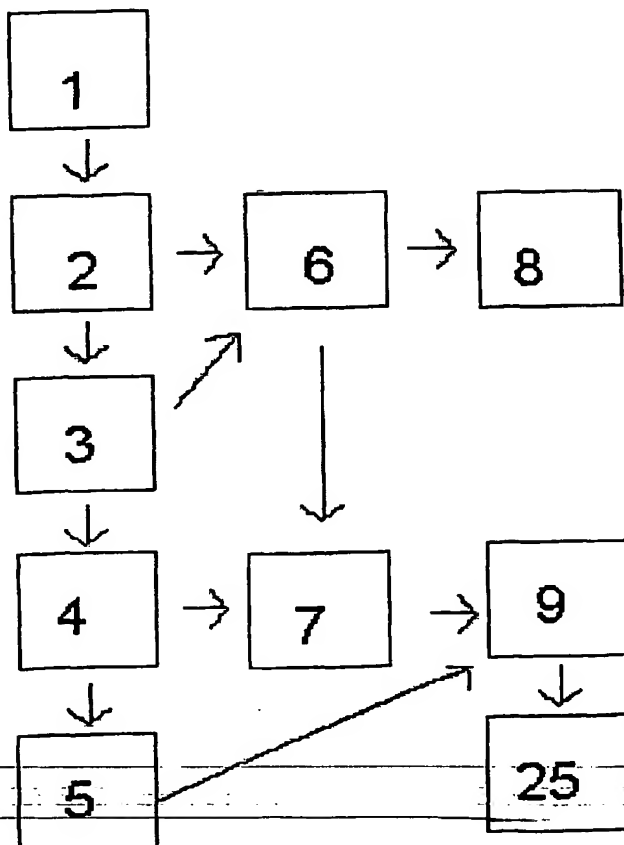
PCT

(10) International Publication Number  
**WO 2004/046279 A1**

- (51) International Patent Classification<sup>7</sup>: **C10J 3/00**, (72) Inventor; and  
C02F 11/00 (75) Inventor/Applicant (for US only): **BRAUER, Peter, Dirk**  
[DE/DK]; Solsortevej 34, DK-8860 Ulstrup (DK).
- (21) International Application Number:  
PCT/DK2003/000787 (74) Agent: **ZACCO DENMARK A/S**; Hans Bekkevolds Allé  
7, DK-2900 Hellerup (DK).
- (22) International Filing Date:  
18 November 2003 (18.11.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
PA200201775 18 November 2002 (18.11.2002) DK
- (71) Applicant (for all designated States except US): **SAMSON**  
**BIMATECH I/S** [DK/DK]; Bjerringbrovej 10, DK-8850  
Bjerringbro (DK).
- (81) Designated States (national): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, EG, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: METHOD OF MANURE SLURRY TREATMENT



(57) Abstract: A method of treating manure wherein the manure is subjected to separation in a fibre fraction and a manure water fraction; said fibre fraction is dried and subjected to gasification; said manure water fraction is subjected to concentration and the produced gasses from said gasification and said concentration are collected and optionally combusted; optionally the manure water fraction is subjected to thermal degradation.

BEST AVAILABLE COPY

FA



(84) Designated States (*regional*): ARIPO patent (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— *with international search report*

## Method of manure slurry treatment

### Field of invention

- 5 This invention relates to an improved method of treating manure slurry and to a new apparatus for treating of manure slurry.

### Background

- 10 Manure slurry and especially manure slurry from pigs forms an increasing problem for many farmers. Neighbours to farms often complain about the smell from manure and as a result of such complaint, the farmers are often constrained in increasing the production.
- 15 Further governmental regulations set limits for how many animals a farmer is allowed to have on a farm with a given agricultural area. Among these regulations are limits on how and when the farmer is allowed to spread the manure on his agricultural area. In certain countries it is not even allowed to spread the manure and therefore the farmer has to get rid of the manure by
- 20 other means. These limits call for increased storage tanks for the manure slurry and often tight regulations for how to store the manure slurry.

- If a farmer intends to increase the number of animals on his farm, he has to increase his agricultural area or be able to treat his manure without
- 25 hampering his neighbours or the environment.

- In the manure there are substantial amounts of substances suitable in fertilizers and that can be used as substitutes for commercially available fertilizers. By isolating these substances from the manure in an essentially
- 30 smell free form it would be possible for the farmer to save expenses to commercial fertilizers and minimize the stored amount of manure.

---

CONFIRMATION COPY

## Prior art

- EP 1 182 248 A1 discloses a method of processing animal manure comprising drying the manure, subjecting the manure to gasification thereby yielding a combustible gas mixture, purifying the gas mixture and cracking the gas mixture. The gasification is carried out at temperatures well above 600°C in order to avoid tar production. This method is mainly suitable in processing relatively dry manure such as manure from chickens.
- 10 Ingeniøren, Friday 14.6.02, number 24 page 14 "Gylleseparator giver renere miljø" discloses a process for treating manure wherein the manure is separated in a fibre fraction and a manure water fraction, said manure water fraction being degassed by heating. The gas is purified for fatty acids and the remaining manure water fraction is concentrated. In this process which is
- 15 merely a concentration process the energy rich fibre fraction is just left unused and the energy in the fatty acids as well.

- Drying manure with a relatively high water content requires too much energy to be economically suitable. Therefore, there is a need for a process which in a cheap and easy way can process both water rich and water poor manure.
- 20

## Summary of the invention

- The inventors have discovered that by separating the manure slurry in a fibre fraction and a water fraction and further processing these fractions, in a special manner the manure slurry can be converted to ashes and water with an energy surplus.
- 25

- According to the invention there is provided a method of treating manure slurry comprising the steps of
- 30

- a) separating the manure slurry in a fraction containing a substantial amount of fibres and a first water fraction essentially consisting of water,  
b) drying said fibre fraction,  
c) subjecting said dried fibre fraction to gasification to form a combustible mixture of gasses,  
5 d) heating the water fraction to an elevated temperature to thermally degrade organic compounds and optionally to evaporate water so as to form a combustible gas mixture and a second water fraction  
e) burning at least a part of the combustible gasses from steps c) and d)  
10 to generate heat for the drying, gasification and/or heating in steps b), c) and d), respectively

By use of this process an essentially manure free pig production is possible and farmers will be able to expand without the problems previously  
15 mentioned. Further the farmer will be able to reduce expenses for heating since the process has an output of hot water.

Further the process can provide the main substances in fertilizers in an essentially pure form thereby giving the farmer the possibility of reducing the  
20 amount of commercial fertilizers.

### **Description of preferred embodiment**

The invention is based on the discovery that by processing manure slurry in the above mentioned manner sufficient energy is generated to allow the  
25 above mentioned processes to be performed without the supply of external energy. Furthermore the method of the invention also makes it possible to recover oil useful in diesel engines, to recover metals and to recover phosphorous compounds, ammonia compounds and potassium compounds.

30

*The separation step*

In a preferred embodiment of the invention the manure slurry is separated in a fibre fraction and a first water fraction by mechanical means e.g. a centrifuge or a press. In an even more preferred embodiment vacuum is used to aid the separation. Optionally a flocculation agent such as alumina based electrolytes, sulphate compounds, polyelectrolytes and humin based compounds; bases such as  $\text{Ca}(\text{OH})_2$  or acids such as  $\text{H}_2\text{SO}_4$  can be added to the manure in order to increase the fibre fraction as much as possible. Furthermore micro bubbles can be used to facilitate the separation.

10

*The drying step*

The fibre fraction from the separation step is dried preferably by means of heat. Preferably the fibre fraction is dried to a dry solid matter content of at least 75%, preferably to a dry solid matter content of at least 80%, more preferred to a dry solid matter content of at least 85%, and most preferred to a dry solid matter content of at least 95%.

15

In a preferred embodiment the drying is performed by means of a combination of heat and vacuum.

20

In another embodiment an Archimedes screw is used during the drying process, thereby achieving a continuous transportation of the fibre fraction through the drier.

Preferably the evaporated product from the drying process is combined with the first water fraction supplied to the heating step, preferably either in an intermediate storage tank, during a thermal degradation step or during a concentration of the water fraction. Optionally possible combustible gasses being in said evaporated product are isolated and condensed or used as fuel.

30

In another preferred embodiment the evaporated product is treated separately in at least one scrubber yielding a combustible gas and a disposable condensate.

5     *The gasification step*

The gasification can be performed at temperatures in the range from 250°C to 900°C. In a preferred embodiment the gasification is performed at temperatures between 400°C and 650°C and most preferred between 500°C and 600°C. The gas produced has an energy content sufficient for running  
10   the process. In one embodiment at least 50% of the fibre mass is converted to gas, preferably at least 60 % and most preferably at least 65%.

When using a temperature above 520°C to 560°C both phosphor and ammonia will mainly be in the gas phase.

15

Each kg of solid matter produces energy equal to 4-4.5 kWh which is bound in the produced gas and the residue from the gasification.

In a preferred embodiment the gasification is performed in a pipe with the  
20   fibres inside and heat for the gasification applied on the outside. Preferably the heat is supplied in a manner to provide a heating rate at 2°C to 7°C per second. Preferably the pipe is made of a chamotte material.

Optionally the gasification is carried out in such a manner that combustible  
25   pyrolysis coal (residue) is an additional product of the gasification step.

The ash from an optional combustion of the residue from the gasification is in the form of a very fine powder which is rich in metals such as Zn, Cu and Ni. Said ash is therefore suitable for the refining industry such as the galvano  
30   industry which is working with a cathode-anode setup depositing the pure metals on the cathode.

In a preferred embodiment the gas produced during the gasification is purified, preferably by use of at least one scrubber. In a more preferred embodiment the gas is purified in two sequential scrubbing processes e.g. by first scrubbing with base such as  $\text{Ca}(\text{OH})_2$  or  $\text{KOH}$  in a first scrubber and afterwards scrubbing with  $\text{H}_2\text{SO}_4$  in a second scrubber. The output of the scrubbing processes is one or more of the following compounds  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ,  $\text{CaCO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Ca}(\text{HSO}_4)_2$ ,  $\text{KHSO}_4$  and  $\text{K}_2\text{CO}_3$ . These compounds can be used as commercial fertilizers.

In another embodiment the produced gas from the gasification step is combined with the gas produced in optional boiling of the first water fraction.

*The Boiling step (thermal degradation)*

In a preferred embodiment of the method the manure water fraction is heated under pressure in order to thermally decompose organic matter. The manure water fraction is heated to above  $95^\circ\text{C}$ , preferably the manure water fraction is heated to above  $120^\circ\text{C}$ , more preferably the water fraction is heated to above  $140^\circ\text{C}$ , most preferably the manure water fraction is heated to between  $140^\circ\text{C}$  and  $160^\circ\text{C}$ . During this thermal decomposition a small amount of combustible gas is produced. In a preferred embodiment this step is performed at an elevated pressure.

In a preferred embodiment acid or base is added to the water fraction in order to aid the thermal decomposition of organic matter and to kill possible bacteria. Preferred acids are strong acids such as  $\text{H}_2\text{SO}_4$  and preferred bases are strong bases such as  $\text{KOH}$ ,  $\text{Ca}(\text{OH})_2$ . In a particularly suitable embodiment the pH is kept above 11 during the boiling.

Addition of acid in this step keeps ammonia in solution and thereby providing the possibility for a later separation, if desired.



The water fraction is preferably concentrated and preferably under reduced pressure. This concentration can be performed in commercially available evaporators. In a preferred embodiment the evaporator reuses the heat in the generated steam to further evaporation, as the skilled person is fully aware of.

In a preferred embodiment the hot water from the concentration is used to heat the production facility e.g. a piggery or a house.

In a preferred embodiment the exit water has a temperature between 85°C and 95°C.

10 In a preferred embodiment the gases from the concentration are scrubbed with acid and base as previously described.

In a preferred embodiment the hot water from the concentration is used to preheat the first water fraction.

#### *The combustible gases*

15 Depending on the desire of the farmer, the combustible gases can be burned and thereby provide the heat for the process plus an excess, or some of the gases can be condensed into pyrolysis oil.

In a preferred embodiment of the invention the light gases are burned as well as some of the heavier in order to run the process. The excess of heavier gasses is condensed to pyrolysis oil which can be stored and used during start up or combusted in diesel engines.

20 In a preferred embodiment the entire process is performed in a closed system except for the combusting of the produced gasses. Thereby it is possible to obtain an essentially smell free manure decomposition.

In an alternative embodiment the manure slurry is pre-treated with heat prior to separation. Optionally thermal degradation is carried out during this pre-treatment.

- 5 In a preferred embodiment the drying step, the gasification step and/or the heating step are carried out at reduced pressure.

The invention will now be describe in further detail with reference to the drawings in which

- Figure 1 shows a flow chart of the main steps in the process.
- 10 Figure 2 shoes a flow chart of the recycling of metals from ashes
- Figure 3 shows a flow chart of the scrubbing sequence
- Figure 4 shows a flow chart of a preferred heat treating of a water fraction
- Figure 5 is an illustration of the flow in an apparatus for carrying out the invention.
- 15 Figure 1 shows one embodiment of the invention, where manure slurry (1) first is separated into a fraction containing fibres and a first water fraction in a filtering unit (2). The fibre fraction is dried in a drier (3) using heat from burned combustible gasses. The dried fibre fraction is subjected to gasification in a gasification unit (4), by use of heat from the burned
- 20 combustible gasses. The gasification results in residue (pyrolysis coal) (5) and a combustible gas (7). The water fraction from the separation unit (2) is subjected to heat (6) resulting in a combustible gas fraction (7) and a second water fraction (8). The combined combustible gasses and optionally the residue from the gasification (5) are burnt in an oven (9) thereby providing
- 25 heat for the drying, the gasification and the heat treatment of the first water fraction. In a preferred embodiment the hot second water fraction (8) is used to pre-heat the first water fraction. The combustion of said residue results in a small amount of ashes (25).

Figure 2 shows the possible refining of the ashes (25) from the gasification. The ashes can by galvano refining be separated in copper (10), zink (11) and nickel (12).

- 5 The combustible gasses (7) can be purified by scrubbing as shown in figure 3. The gasses are first scrubbed in a first scrubber (13) with  $\text{Ca}(\text{OH})_2$  resulting in a mixture of  $\text{Ca}(\text{H}_2\text{SO}_4)_2$  and  $\text{CaCO}_3$  (14). Secondly the gasses are scrubbed in a second scrubber (15) with  $\text{H}_2\text{SO}_4$  resulting in  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  (16) and a purified gas mixture (17). This scrubbing sequence
- 10 can be performed on the each of the combustible gas mixtures before combining or the scrubbing can be done on the combined gas mixture (7). Figure 4 shows an embodiment where the first water fraction from the filtering unit (2) is subjected to a first heat treatment (6) at elevated pressure. During this heating thermal degradation of fatty acids etc takes place. After the
- 15 degradation the manure water fraction is concentrated in an evaporator (18) resulting in a concentrated potassium fraction (20) and a mixture of combustible gasses and steam. Said mixture is purified in a sequence as shown in figure 3 resulting in purified gas (17) and a hot second water fraction (8)
- 20 The gasses obtained from the gasification are scrubbed twice, first with  $\text{Ca}(\text{OH})_2$  and secondly with  $\text{H}_2\text{SO}_4$  and then directed to an oven where they are burned thus creating heat for the process. The ashes from the gasification are subjected to galvano purification.

Figure 5 is an illustration of a plant for carrying out the method.

## Patent Claims:

1. A method of treating manure slurry comprising the steps of
- 5 a) separating the manure slurry in a fraction containing a substantial amount of fibres and a first water fraction essentially consisting of water,
- b) drying said fibre fraction,
- c) subjecting said dried fibre fraction to gasification to form a combustible mixture of gasses,
- 10 d) heating the water fraction to an elevated temperature to thermally degrade organic compounds and optionally to evaporate water so as to form a combustible gas mixture and a second water fraction
- e) burning at least a part of the combustible gasses from steps c) and d) to generate heat for the drying, gasification and/or heating in steps b), c) and d), respectively.
- 15
2. A method according to claim 1, wherein a fraction of said combustible gasses is condensed so as to recover oil.
3. A method according to claim 1 or 2, wherein said combustible gasses are
- 20 purified.
4. A method according to any one of claims 1 to 3, wherein said combustible gasses are scrubbed in at least one scrubber, preferably with  $\text{Ca}(\text{OH})_2$  and/or  $\text{H}_2\text{SO}_4$ .
- 25
5. A method according to any one of claims 1 to 4, wherein the residues from the gasification are burned.
6. A method according to any one of claims 1 to 5, wherein said first water
- 30 fraction during thermal degradation is heated to above  $95^\circ\text{C}$ , preferably

heated to above 120°C, more preferably heated to above 140°C, most preferably heated to between 140°C and 160°C.

7. A method according to any one of claims 1 to 6, wherein the evaporated product from said drying step is combined with the water fraction supplied to  
5 the heating step.

8. A method according to any one of claims 1 to 7 wherein the heating step comprises two steps, viz. a degradation step and a concentration step.

9. A method according to 8, wherein said concentration is carried out at reduced pressure.

10 - 10. A method according to any one of claims 1 to 9, wherein said gasification is performed at temperatures in the range from 250°C to 900°C, preferably at temperatures between 400°C and 650°C and most preferably at temperatures between 500°C and 600°C.

Figure 1

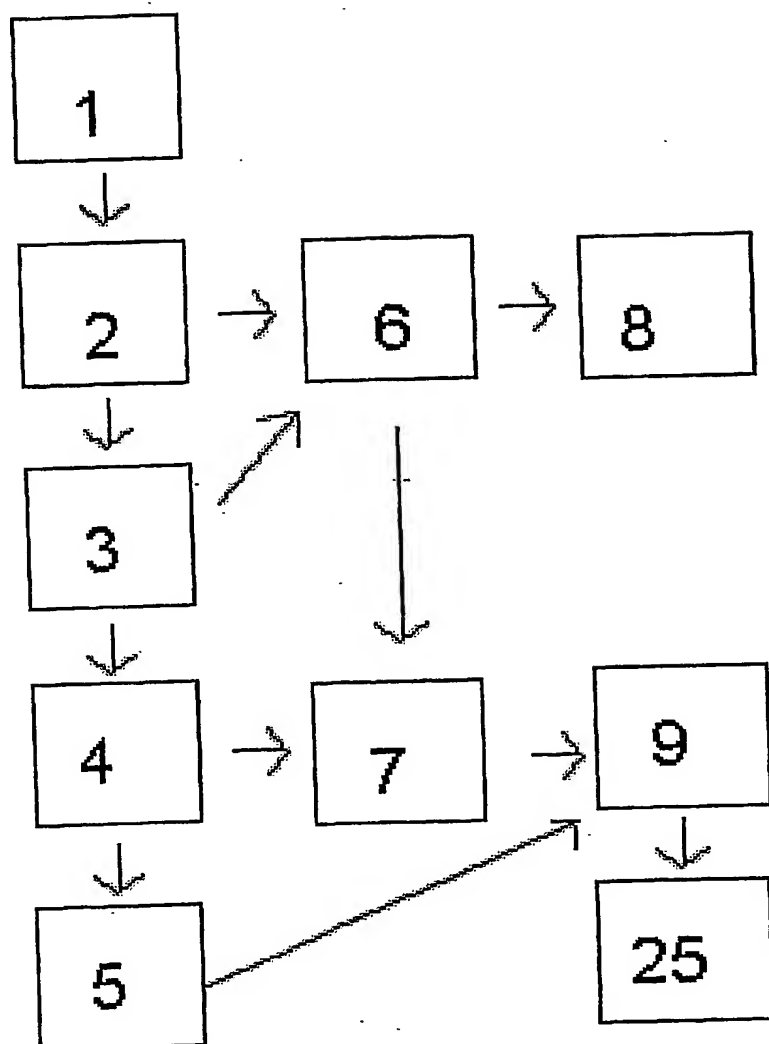


Figure 2

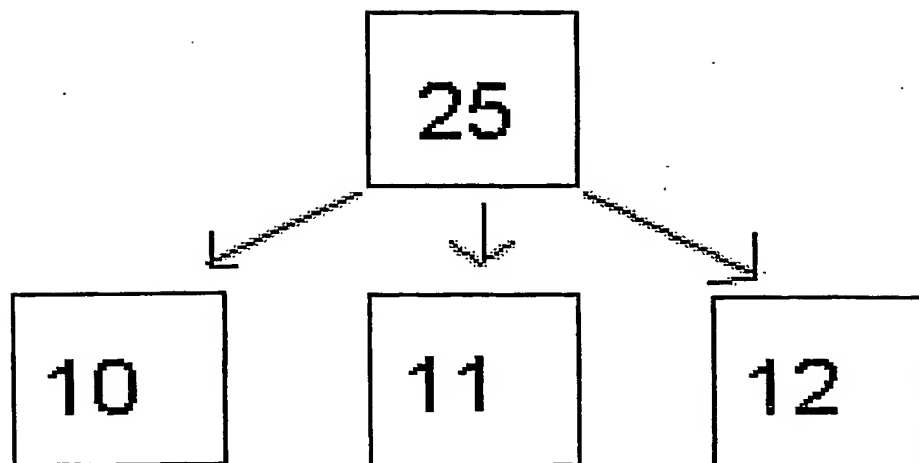


Figure 3

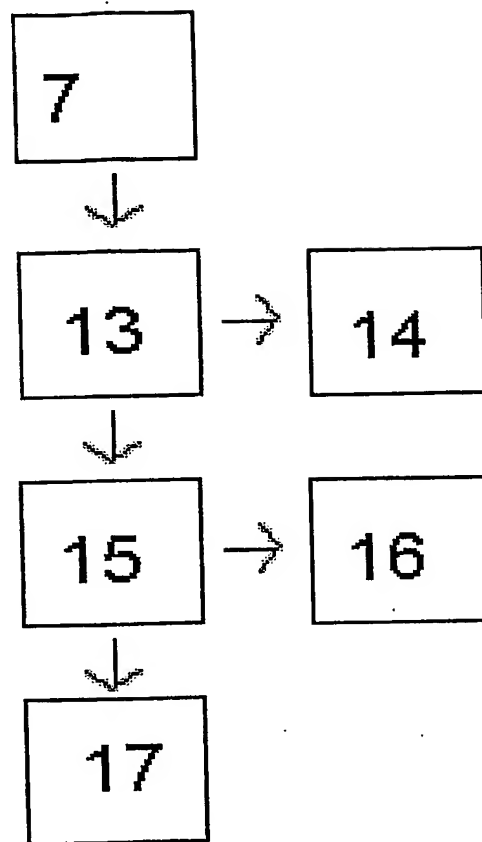
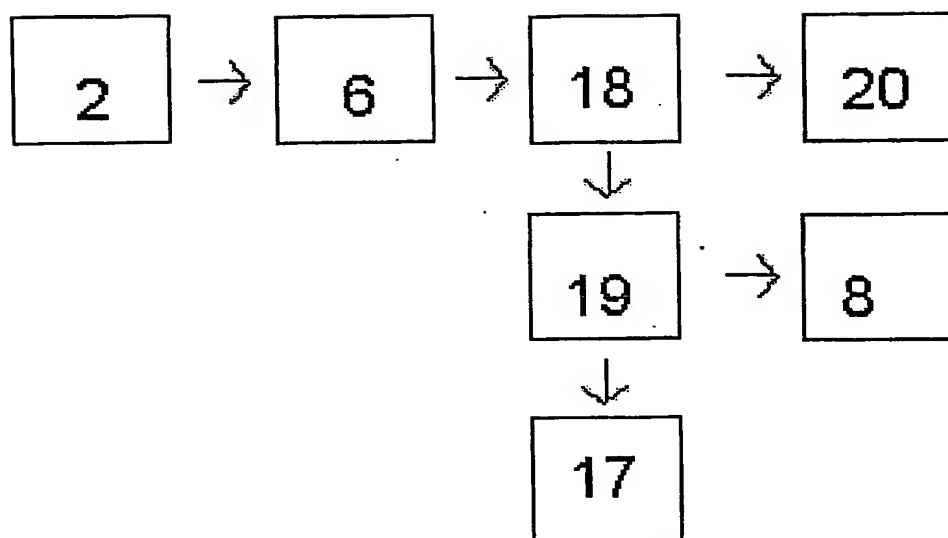




Figure 4





# INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 03/00787

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C10J3/00 C02F11/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C10J C02F F23G C05F C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 005, no. 111 (C-063), 18 July 1981 (1981-07-18) & JP 56 051292 A (HITACHI PLANT ENG & CONSTR CO LTD), 8 May 1981 (1981-05-08) abstract	1-10
A	WO 99 42423 A (BIOSCAN AS ;NORDDAHL BIRGIR (DK)) 26 August 1999 (1999-08-26) figure 1 abstract	1-10
A	LISE MÖLLER AARUP: "Gylleseparator giver renere miljø" INGENJÖREN, vol. 24, June 2002 (2002-06), XP002272974 page 14	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "Z" document member of the same patent family

Date of the actual completion of the international search

10 March 2004

Date of mailing of the international search report

01 04 2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

MÄRTEN HULTHÉN / ELY

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/DK 03/00787

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 607 644 A (TEXACO DEVELOPMENT CORP) 27 July 1994 (1994-07-27) abstract	1-10
A	--- EP 1 182 248 A (B T G B V) 27 February 2002 (2002-02-27) abstract	1-10
A	--- US 4 198 211 A (SHATTOCK GEOFFREY F) 15 April 1980 (1980-04-15) abstract	1-10
A	--- PATENT ABSTRACTS OF JAPAN vol. 013, no. 579 (C-668), 20 December 1989 (1989-12-20) & JP 01 242185 A (KEMIKARUMAN:KK), 27 September 1989 (1989-09-27) abstract -----	1-10

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/DK 03/00787

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 56051292	A	08-05-1981	NONE	
WO 9942423	A	26-08-1999	WO 9942423 A1	26-08-1999
			AU 5983298 A	06-09-1999
			CA 2346706 A1	26-08-1999
			CN 1284938 T	21-02-2001
			EP 1056691 A1	06-12-2000
			JP 2002511832 T	16-04-2002
			US 6368849 B1	09-04-2002
EP 0607644	A	27-07-1994	CA 2086212 A1	24-06-1994
			JP 2741565 B2	22-04-1998
			JP 6246297 A	06-09-1994
			US 5211724 A	18-05-1993
			EP 0607644 A1	27-07-1994
			DE 69312250 D1	21-08-1997
			DE 69312250 T2	30-10-1997
EP 1182248	A	27-02-2002	NL 1016019 C2	26-02-2002
			EP 1182248 A1	27-02-2002
US 4198211	A	15-04-1980	GB 1595803 A	19-08-1981
			BE 885575 A7	02-02-1981
			DE 2800666 A1	20-07-1978
			FR 2376827 A1	04-08-1978
			JP 53111303 A	28-09-1978
			SE 7714973 A	08-07-1978
JP 01242185	A	27-09-1989	NONE	

**THIS PAGE BLANK (USPTO)**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☒ **BLACK BORDERS**

☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

☐ **FADED TEXT OR DRAWING**

☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**

☐ **SKEWED/SLANTED IMAGES**

☒ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**

☐ **GRAY SCALE DOCUMENTS**

☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**

☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**